

12

EUROPEAN PATENT APPLICATION

21 Application number: 87303528.1

51 Int. Cl.4: C 01 B 33/18

22 Date of filing: 22.04.87

30 Priority: 24.04.86 GB 8610024

43 Date of publication of application:
28.10.87 Bulletin 87/44

64 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI NL SE

71 Applicant: UNILEVER PLC
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ (GB)

84 Designated Contracting States: GB

71 Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam (NL)

84 Designated Contracting States:
BE CH DE ES FR GR IT LI NL SE AT

72 Inventor: Garvey, Michael Joseph
"The Hollies" Nigel Road
Heswall Wirral Merseyside L60 1XU (GB)

Griffiths, Ian Charles
24 Quarry Avenue
Bebington Wirral Merseyside L63 3HS (GB)

74 Representative: Thomas, Susan Margaret et al
UNILEVER PLC Patents Division P.O. Box 68 Unilever
House
London EC4P 4BQ (GB)

The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

54 Porous silica structures.

57 This invention discloses novel, porous silica structures prepared from silica platelets. The structures are preferably prepared by spray-drying.

BEST AVAILABLE COPY

EP 0 243 165 A2

Description

POROUS STRUCTURES

This invention relates to macroporous silica structures and to processes for their preparation. More particularly the invention relates to macroporous structures formed from mesoporous silica plates.

In USP 2 801 902 Alexander et al disclosed a process for the preparation of planar aggregates or mesoporous silica platelets which are platelets of silica spheroids which were produced from silica sols containing a trace amount of cationic surfactant. In their specification Alexander et al suggest that the aggregation occurs by a process of preferential, directional aggregation of the silica spheroids in the bulk of the dispersion.

The present inventors suggest that the process of aggregation of silica spheroids into apparently planar aggregates is a consequence of the partial hydrophobing of the negatively-charged silica by the adsorbed cationic surfactant and the subsequent adsorption, or deposition, of the silica particles at a gas, oil or hydrophobic solid interface, to form a compact monolayer of silica spheroids. It is thought that these silica spheroids subsequently gel to form a monolayer replica of the interface at which they have been formed. Agitation of the dispersion to rupture the interface, or to detach the monolayer from a hydrophobic substrate, which constitutes an interface, would create a fresh interface for further gelation, resulting in the eventual conversion of the silica sol to silica platelets. It is thought, therefore, that the platelets or aggregates are broken replicas of the interface. The interface may or may not be planar, but since the geometry of the interface is, in general, large in comparison with the fractured replica aggregates, these aggregates appear essentially planar in structure and, hence, may be referred to as platelets.

Accordingly, the present invention provides spheroidal porous silica structures having both macro- and mesopores and comprising a cluster of silica platelets, said platelets generating the macropores in the spaces between them and the mesopores being generated by the spaces between the silica particles forming the platelets, said mesopores interlink the macropores.

The dimensions of the spheroidal clusters of silica platelets will have a mean diameter dependent on the conditions of processing but would typically be less than 250µm. The platelets which form the structure may be prepared in accordance with the general disclosure by Alexander et al in US Patent No. 2 801 902, but can more readily and effectively be prepared by methods which generate a large interface, such as by refluxing vigorously, aeration, or by the use of a falling film reactor or the like.

The dimensions of the silica particles constituting the platelets are generally less than 1µm and preferably in the range 5nm to 100nm, more preferably 5nm to 50nm. Suitably the silica particles are spheroidal and of a uniform size.

The dimensions of the mesopores are determined

by the dimensions of the silica particles constituting the platelets. For close packed monodispersed silica particles which are spheroidal in shape, the minimum size of the interstitial mesopore is given by the following equation:

$$a = 0.732r$$

in which a is the maximum width across the centre of the mesopore and r is the radius of the spheroidal silica particle. The maximum size of the interstitial pores will be determined by the packing of the particles. Suitably however the packing is such that the interstitial mesopores having a maximum size of about $6r$, more suitably about $4r$. Thus for spheroidal particles having a diameter within the range 5nm to 100nm, the meso interstitial pores for monodisperse platelets will be in the range from about 2 to about 200nm.

If the particles are not spheroidal or monodisperse then the average size of the mesopores will be reduced but will be readily measurable by electron microscopy or mercury porosimetry.

The minimum macropore size or inter-platelet size, corresponding to parallel plate contact is for monodisperse spheroidal particles given by the above expression. The maximum macropore size will be determined by the extent of loose packing of the platelets and will approximate to the maximum width of the platelets. This size would typically be less than 20µm. In practice due to the random packing of the plates, which themselves will probably be buckled and creased, the interplatelet distance will probably lie in the range 0.2µm to 15µm, preferably 1 to 15µm.

This invention also provides a process for preparation of the novel porous silica structures comprising spray-drying a slurry of silica platelets. Spray-drying is carried out with an air flow at a temperature from 130°C to 400°C and a silica platelet dispersion at a silica concentration of less than 20% w/w.

The slurry may contain additional materials to modify aggregation behaviour. Such materials would typically be a mineral acid although other species may be used. The spheroidal clusters of platelets so produced can subsequently be strengthened by heating, preferably in a furnace at a temperature between 500 and 1,100°C.

In a preferred form of the process the silica concentration is in the range 5% to 15% w/w.

As described above the silica platelets forming part of the slurry can be formed in accordance with the general disclosure by Alexander et al in US Patent No. 2801902 or by a number of other methods. In general however the platelets are readily formed by generating an aqueous sol containing 0.1 to 10wt% of colloidal silica and mixing therewith a small amount e.g. 0.0003 to 0.03wt% of a cationic surfactant. Preferred cationic surfactants are organic nitrogen bases e.g. cetyl trimethyl ammonium bromide. The platelets form at for example the interface between the sol surface and air.

The present structures can incorporate material in addition to silica. In particular the present structures

can be made from platelets comprising positively-charged silica particles consisting of a dense silica core coated with a poly-valent metal-oxygen compound such as alumina. The platelets can be formed in a manner analogous to that described above but using an anionic surfactant. Further details are given in our co-pending application of even date claiming priority from GB 86 10023.

The present invention thus provides spheroidal silica structures having a predetermined porous structure and a large internal surface area. Due to their structure the material can find uses as a carrier or support. Examples of such uses include chromatographic supports, bioseparation media and catalytic support.

Embodiments of the present invention will now be described with reference to the following Examples which are by way of example only and the following drawings; wherein:

Figures 1 to 6 are plots of log pore diameter in μm against pore volume in $\text{cm}^3 \text{g}^{-1}$ for the products of Examples 1 to 5.

Example 1

An aqueous slurry of platelet silica was prepared by boiling under reflux, for 5 hours, a dispersion containing colloidal silica (Ludox HS40, 5.3% w/w SiO_2) and cetyltrimethyl ammonium bromide (0.015% w/w).

3 kg of slurry were fed into the spray dryer at a rate of $800 \text{ cm}^3 \text{ min}^{-1}$. The operating conditions of the spray dryer were as follows:

Inlet temperature 318°C

Outlet temperature 134°C

Atomiser speed 16245 rpm

110g of spray-dried solid were collected. The material was examined by scanning electron microscopy and shown to consist of particles in the size range 4-125 microns (50% > 38 microns) with an internal structure commensurate with a cluster of silica platelets.

The material had a total pore volume of $1.5 \text{ cm}^3 \text{g}^{-1}$, determined by mercury porosimetry and a pore size distribution as shown in Figure 1. The surface area determined by nitrogen adsorption was $150 \text{ m}^2 \text{g}^{-1} \pm 10\%$.

Example 2

An aqueous slurry of platelet silica was prepared by boiling under reflux, for $6\frac{1}{2}$ hours, a dispersion containing colloidal silica (Ludox HS40, 7.9% w/w SiO_2) and cetyl trimethyl ammonium bromide (0.022% w/w). The pH of the resulting platelet slurry was reduced from 10.2 to 6.6 by the addition of hydrochloric acid.

3kg of slurry were fed into a spray dryer at a rate of $800 \text{ cm}^3 \text{ min}^{-1}$. The operating conditions of the spray dryer were as follows:

Inlet temperature 306°C

Outlet temperature 144°C

Atomiser speed 16620 rpm

142g of spray-dried solid were collected. The material was examined by scanning electron microscopy which showed particles in the size range 4 to 125 microns and an internal structure as described

In Example 1.

The material had a total pore volume of $1.7 \text{ cm}^3 \text{g}^{-1}$, determined by mercury porosimetry on particles sieved to a size range of >38 to <125 microns, and a pore size distribution as shown in Figure 2. The surface area determined by nitrogen adsorption was $150 \text{ m}^2 \text{g}^{-1} \pm 10\%$.

Example 3

The spray-dried material prepared in Example 2 was sieved to give particles of size >45 microns and <75 microns. This material was calcined at 600°C for 2 hours. Examination by scanning electron microscopy showed an internal structure as described in Example 1.

The total pore volume, determined by mercury porosimetry was $1.6 \text{ cm}^3 \text{g}^{-1}$, and a pore size distribution as shown in Figure 3. The surface area, determined by nitrogen adsorption was $150 \text{ m}^2 \text{g}^{-1} \pm 10\%$.

Example 4

An aqueous slurry of platelet silica was prepared by boiling under reflux, for $4\frac{1}{2}$ hours, a dispersion containing colloidal silica (Ludox HS40, 7.3% w/w SiO_2) and cetyl trimethyl ammonium bromide (0.02% w/w).

192kg of slurry were removed from the reactor and the slurry pH reduced from 10.2 to 6.8 by the addition of sulphuric acid. This slurry was fed into a spray dryer at the rate of $800 \text{ cm}^3 \text{ min}^{-1}$, and the operating conditions of the spray dryer were as follows:

Inlet temperature 335°C

Outlet temperature 132°C

Atomiser speed 16265 rpm

13 kg of the spray-dried solid were collected. Examination by scanning electron microscopy revealed an internal structure as described in Example 1.

The material had a total pore volume of $1.5 \text{ cm}^3 \text{g}^{-1}$, determined by mercury porosity and a pore size distribution as shown in Figure 4. The surface area determined by nitrogen adsorption was $123.6 \text{ m}^2 \text{g}^{-1}$.

The remaining slurry was boiled under reflux for a further $4\frac{1}{2}$ hours. The pH of the dispersion was reduced from 10.2 to 7.2 by the addition of sulphuric acid and 148kg were fed into a spray-dryer, at a rate of $800 \text{ cm}^3 \text{ min}^{-1}$. The operating conditions of the spray-dryer were as follows:

Inlet temperature 320°C

Outlet temperature 135°C

Atomiser speed 16045 rpm

8kg of spray-dried solid were collected. 2kg of this material were classified (Alpine classifier) into two fractions, the upper size fraction (400g) containing particles 80% of which were between 40 and 90 microns. Examination of this material by scanning electron microscopy revealed an internal structure as described in Example 1.

The material had a total pore volume, determined by mercury porosimetry of $1.7 \text{ cm}^3 \text{g}^{-1}$ and a pore size distribution as shown in Figure 5.

Example 5

A sample of the upper size fraction spray-dried material prepared in Example 4 was calcined at 860°C for 2 hours.

Examination by scanning electron microscopy revealed an internal structure as described in Example 1.

The material had a total pore volume of 1.6cm³ g⁻¹ determined by mercury porosimetry, and a pore size distribution as shown in Figure 6.

The surface area determined by nitrogen adsorption was 70m²g⁻¹ ± 10%.

Claims

1. Spheroidal porous silica structures having both macro- and mesopores and comprising a cluster of silica platelets, said platelets generating the macropores in the spaces between them and the mesopores being generated by the spaces between the silica particles forming the platelets, said mesopores interlink the macropores.

2. Spheroidal porous silica structures as claimed in claim 1, having macropores of less than 20µm.

3. Spheroidal porous silica structures as claimed in claim 1 or claim 2 having macropores greater than about 0.2µm.

4. Spheroidal porous silica structures as claimed in any one of the preceding claims having mesopores in the range of from about 2nm to about 200nm.

5. Spheroidal porous silica structures as claimed in any one of the preceding claims wherein each platelet comprises substantially monodispersed spheroidal silica particles.

6. A process for the preparation of porous silica particles as claimed in any one of the preceding claims comprising spray-drying a slurry of silica platelets.

7. A process as claimed in claim 6 in which the spray-drying is carried out with an air flow at a temperature from 130°C to 400°C from a platelet dispersion having a silica concentration of less than 20% w/w.

8. A process as claimed in claim 7 in which the slurry has a silica concentration between 5 and 15% w/w.

9. A process as claimed in any one of claims 6 to 8 including subsequently heating the silica platelets formed.

0243165
Fig. 1.

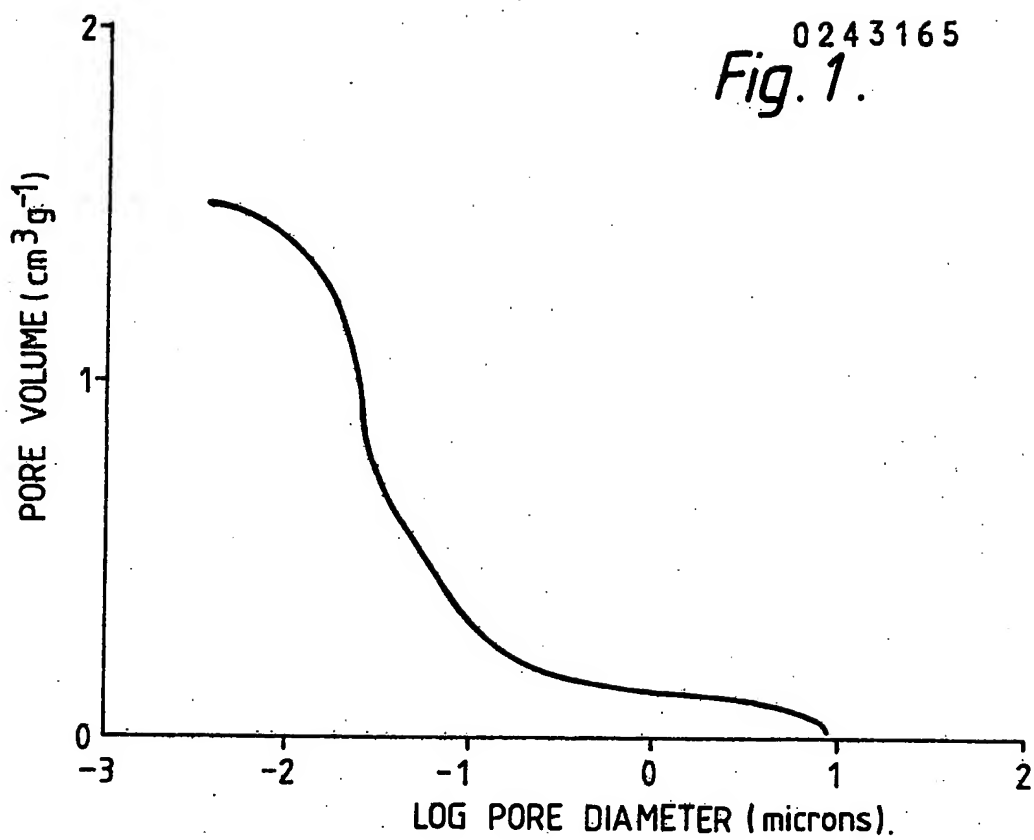
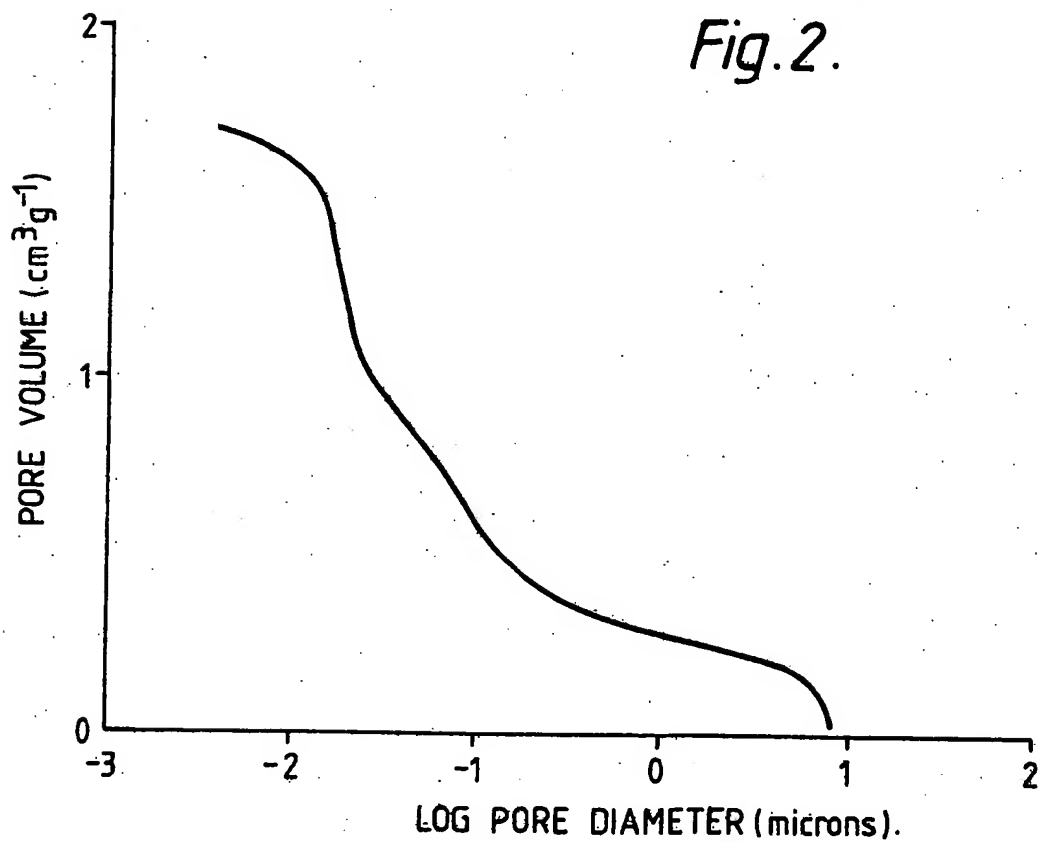


Fig. 2.



0243165

Fig.3.

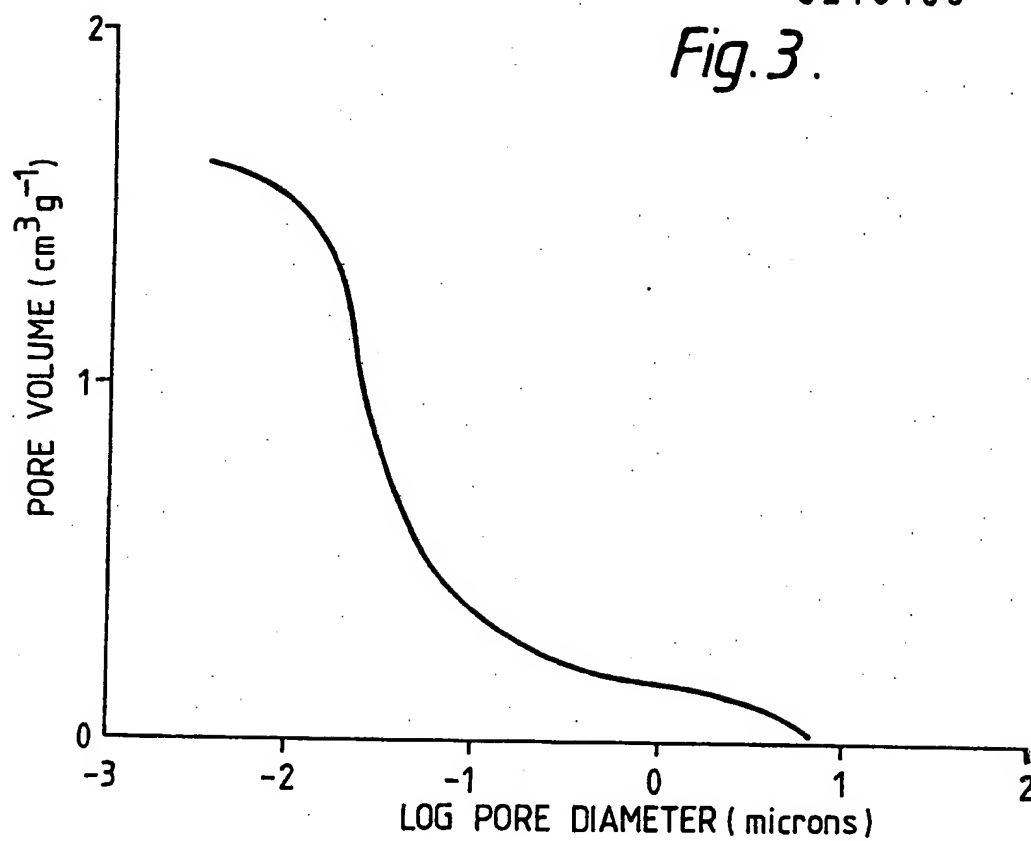
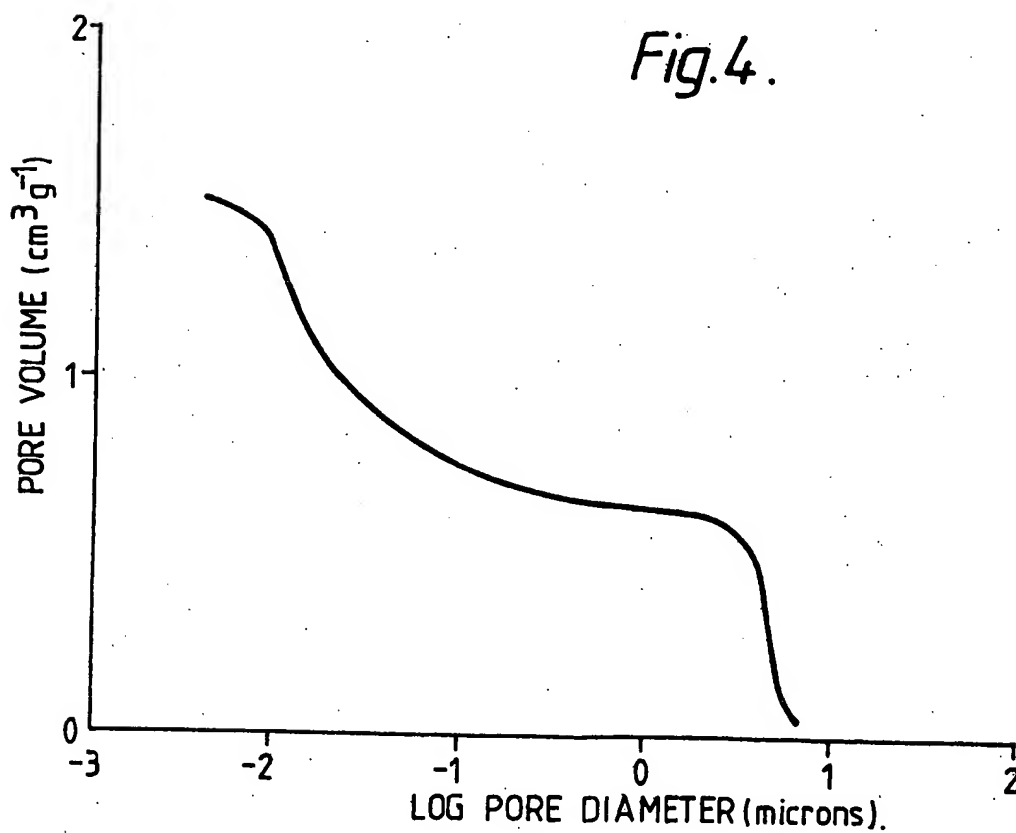


Fig.4.



0243165

Fig. 5.

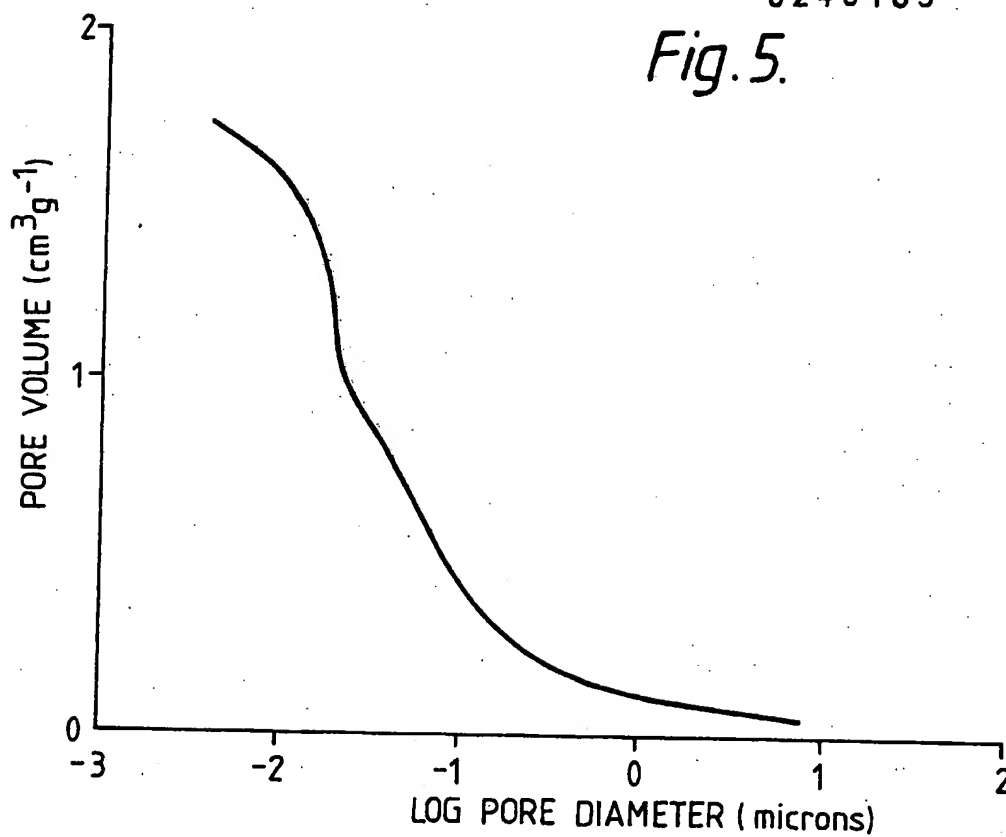
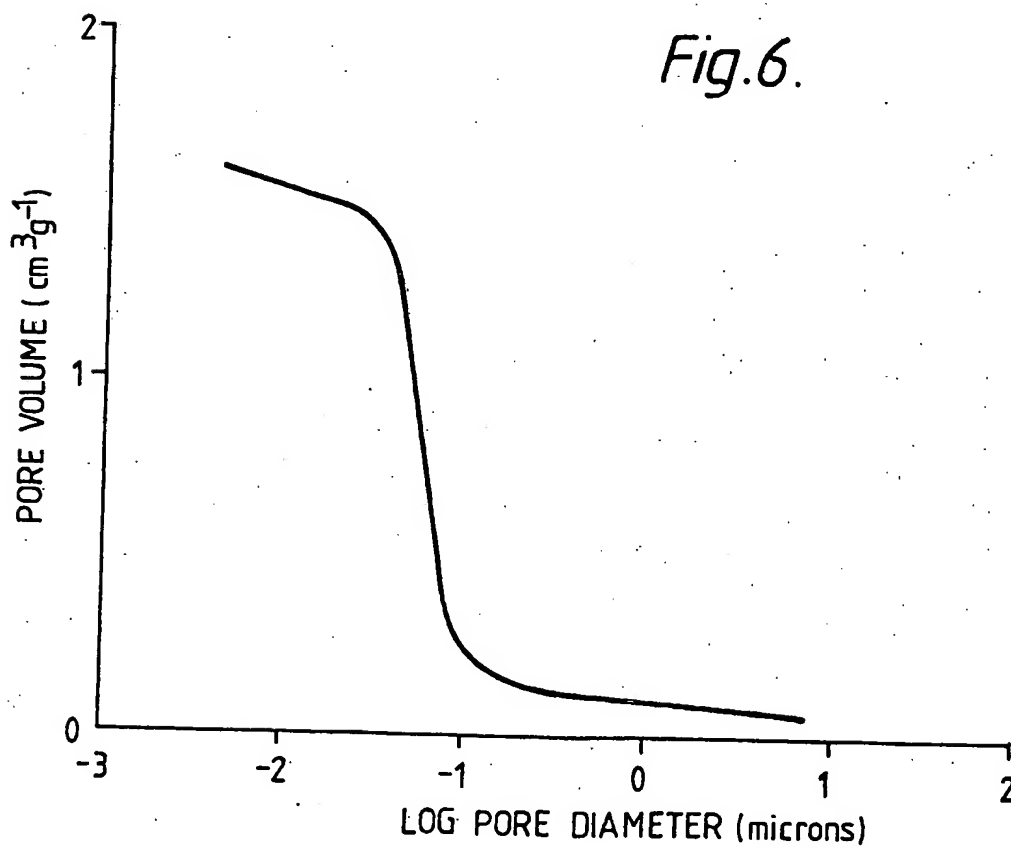


Fig. 6.



(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 243 165
A3**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87303528.1

(51) Int. Cl.⁵: **C01B 33/18**

(22) Date of filing: 22.04.87

(30) Priority: 24.04.86 GB 8610024

(43) Date of publication of application:
28.10.87 Bulletin 87/44

(64) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI NL SE

(88) Date of deferred publication of the search report:
14.03.90 Bulletin 90/11

(71) Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

(64) **GB**

Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

(64) **BE CH DE ES FR GR IT LI NL SE AT**

(72) Inventor: Garvey, Michael Joseph
"The Hollies" Nigel Road
Heswall Wirral Merseyside L60 1XU(GB)
Inventor: Griffiths, Ian Charles
24 Quarry Avenue
Bebington Wirral Merseyside L63 3HS(GB)

(74) Representative: Thomas, Susan Margaret et al
UNILEVER PLC Patents Division P.O. Box 68
Unilever House
London EC4P 4BQ(GB)

(54) **Porous silica structures.**

(57) This invention discloses novel, porous silica structures prepared from silica platelets. The structures are preferably prepared by spray-drying.

EP 0 243 165 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 30 3528

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A,D	US-A-2 801 902 (G. B. ALEXANDER et al.) * claim 1 * ---	1	C 01 B 33/18
A	GB-A-1 416 139 (UNILEVER LTD.) * column 2, lines 21-55 * ---	6	
A	DE-B-2 505 191 (DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT) * claim 1 * ---	6	
A	PATENT ABSTRACTS OF JAPAN vol. 2, no. 100 (C-78)(1837), 18 August 1978; & JP - A - 53 65293 (CENTRAL GLASS K.K.) 10.06.1978 ---	6	
A	EP-A-0 050 902 (STAMICARBON B.V.) * page 6, line 19 - page 7, line 16; claim 1 * -----	6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 01 B 33/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 28-11-1989	Examiner CLEMENT J.P.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.